Location: SOP Files
QA Officer's Office
Wet Chemistry Laboratory

1.0 SCOPE

1.1 This SOP is applicable to drinking, surface, and saline water, domestic and industrial wastes.

1.2 The SOP is suitable for all concentration ranges of hardness; however, in order to avoid large titration volumes, use a sample aliquot containing not more than 25-mg $CaCO_3$.

2.0 SUMMARY OF THE METHOD

2.1 This SOP is a procedure for evaluating Total Hardness as $CaCO_3$ in liquid samples.

2.2 Calcium and magnesium ions in the sample are sequestered upon the addition of disodium ethylenediamine tetraacetate (Na_2EDTA). The end point of the reaction, using indicator, has a red color in the presence of Ca and Mg and a blue color when they're sequestered.

3.0 INTERFERENCES

3.1 When in excessive amounts, some heavy metal ions interfere by causing fading or indistinct end points.

4.0 APPARATUS AND MATERIALS

4.1 Digital titrator
4.2 Stir plate
4.3 Clear plastic cups
4.4 Stir Bar
4.5 Graduated Cylinder
4.6 Pipette
4.7 Analytical Balance

5.0 REAGENTS

5.1 Deionized (DI) water
5.2 0.080 EDTA tetrasodium titration cartridge
5.3 0.800 EDTA tetrasodium titration cartridge, used for samples of known or suspected high concentration
5.4 Hach Buffer Solution Hardness 1
5.5 Hach ManVer® 2 Hardness indicator powder pillows
5.6 10,000 mg/L calcium, total hardness as $CaCO_3$ standard
5.7 5N Sodium Hydroxide (NaOH)

6.0 SAMPLE HANDLING AND PRESERVATION

6.1 Hardness is best analyzed as soon as possible from the time the sample is collected. Holding time for water samples is 180 days refrigerated at 4 ± 2^oC

6.2 Samples must be provided in unpreserved, clear plastic bottles. When samples are received in Nitric acid preserved bottles, samples must be neutralized with NaOH before analysis.

7.0 PROCEDURE

7.1 Color Development and Measurement

7.1.1 Pour 100 mL of DI water in a clear plastic cup to make a Blank sample.

7.1.2 Place a magnetic stirring bar in the cup and place the cup on a stir plate. Turn on stir place so that the sample is stirred well, but its color is still clearly visible.

7.1.3 Add 1.0 mL buffer solution to sample.

7.1.4 Pour one Hach ManVer® 2 Hardness indicator powder pillow in the cup.

7.1.5 Using a digital titrator set up with a 0.080 EDTA tetrasodium titration cartridge, place its tip in the sample so that the acid may be released into the sample. Slowly turn the end piece clockwise until the water just turns from its original pink color to blue.

7.1.6 The number of digits used to do this is the value for the Blank. This value will be subtracted from the digit values of all other samples.

7.1.7 Rinse off magnetic stir bar.

7.1.8 Analyze quality control samples by following Sections 7.1.2 to 7.1.7.

7.1.9 Place 10 mL of a sample in another cup and add 90 mL DI water to it. Repeat Sections 7.1.2 to 7.1.7 to find the number of digits needed to titrate the sample. If this value is exceedingly small or large, the dilution of the sample may be adjusted

8.0 CALCULATIONS

8.1 Hardness mg $CaCO_3$/L = $\frac{D*100mL}{S}\times M$

Where D = number of Digits used in titration of sample
M = multiplier number specified by concentration of cartridge (in this case, 1.0)
S = mL of sample used

9.0 QUALITY CONTROL

9.1 See Table 1

9.2 Samples are analyzed in batches of twenty or less per QC set. The QC samples that are analyzed per batch are:

- Control
- MS
- LCS
- DUP
- MSD (optional if set is not Level 3)
- Method Blank
- Blank Spike

Table 1. Quality Control Requirements (Sample Set = 20 samples)

QC Analysis	Required/ Frequency	Limits	Corrective Action	Corrective Action after Reanalyzing
Method (preparation) Blank	Yes One each set	<MDL or 1/10 Regulatory limit	Remove contamination and rerun	Notify Client. Flag Data.
Laboratory Control Sample (LCS)	Yes One each set	90%-110%	Rerun	Notify Client. Flag Data.
Blank Spike	Yes One each set	90%-110%	Rerun	Notify Client. Flag Data.
Control	Yes One each set	90%-110%	Rerun	Notify Client. Flag Data.
Matrix Duplicate	Yes One each set	RPD<20%	Rerun entire set	Notify Client. Flag Data.
Matrix Spike	Yes One each set	80%-120%	Analyze by Method of Standard Additions	Notify Client. Flag Data.
Matrix Spike Duplicate	Level 3 One each set	80%-120%	Analyze by Method of Standard Additions	Notify Client. Flag Data.

10.0 DOCUMENTATION

10.1 Hardness Bench Sheet

10.1.1 Analyst
10.1.2 Date Run
10.1.3 Method #
10.1.4 Detection Limit
10.1.5 Program #
10.1.6 Wavelength

10.1.7 Titrant
10.1.8 Merit #
10.1.9 Dilution
10.1.10 Digit Multiplier
10.1.11 Digits
10.1.12 Total Solids %
10.1.13 Final Concentration (mg/L)
10.1.14 Spike (mg/L)
10.1.15 % Recovery
10.1.16 Source/Lot #
10.1.17 Run Time

11.0 METHOD PERFORMANCE

11.1 Precision and accuracy studies are performed on as needed basis. (Ex. new instrument, etc.)
11.2 Method Detection limit studies are performed annually.

12.0 REFERENCES

12.1 EPA Water NPDES, Method 130.2, EPA Test Methods, Revision 1982, Hardness, Total (mg/L as $CaCO_3$, Titrimetric, EDTA)
12.2 Standard Methods, Method 2340, 20th Edition.

13.0 SAFETY

13.1 Every Laboratory area has eyewash, emergency shower, and fire extinguisher. The metals lab also has dust masks available for use with dust samples.
13.2 The air system through out the laboratory area is on a 100% fresh air exchange system, this system exchanges 100% the air in the laboratory area with air from outside 6 times per hour and 30 times per hour when the emergency purge button is hit.
13.3 A reference file of material safety data sheets (MSDSs) is available to all personnel.
13.4 Specific attention be paid (but not limited) to
13.4.1 Sodium hydroxide is corrosive, causes burns to any area of contact, can slowly pick up moisture from air and react with carbon dioxide from air to form sodium carbonate, and in contact with acids and organic halogen compounds, especially trichloroethylene, sodium hydroxide may causes violent reactions.

14.0 WASTE DISPOSAL AND POLLUTION PREVENTION

14.1 All laboratory waste must be managed, stored, and disposed in accordance with all federal and state laws and regulations.
14.2 Additional information can be found in the Sample Disposal SOP and Merit's Waste Management Plan and Handbook.

15.0 APPROVAL & ISSUE:

15.1 This section indicates which personnel have read, accepted and approved the SOP. All analysts involved with the SOP should acknowledge their comprehension of the SOP with a signature and a date.

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Analyst Date

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Andy Ball, QA Officer Date

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Maya V. Murshak, Technical Director Date